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(54) Title: VOLATILE METALS CAPTURE FROM GAZEOUS STREAMS

(57) Abstract

The invention relates to a process for removing volatile metals from a synthesis gas stream by (a) contacting in a contacting zone a synthesis gas stream containing zinc, lead, mercury, and cadmium with a polysulfide-containing solution under conditions to convert the zinc, lead, mercury, and cadmium; (b) thus producing the respective metal sulfides of the zinc, lead, mercury, and cadmium; and (c) recovering the synthesis gas having reduced amounts of zinc, lead, mercury, and cadmium.

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DESCRIPTIONVOLATILE METALS CAPTURE FROM GASEOUS STREAMSTechnical Field

The invention relates to a process for removing volatile metals from a coal gasification synthesis gas stream.

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Background Art

The presence of volatile metals, both elemental metals and metal compounds, in various gaseous streams is undesirable since it creates an environmental hazard and the volatile metals are a contaminant. In particular, gas streams derived from the gasification of coal generally have minor quantities of zinc, lead, mercury, cadmium, and other metals which must be removed or minimized before the gas is utilized.

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Accordingly, it would be advantageous to have a practical and efficient procedure for removing volatile metals from a gas stream, particularly a coal gasification synthesis gas stream.

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The invention therefore is a process for removing volatile metals from a synthesis gas stream by (a) contacting in a contacting zone a synthesis gas stream containing zinc, lead, mercury, and cadmium with a polysulfide-containing aqueous solution under conditions to convert the zinc, lead, mercury, and cadmium to their respective metal sulfides; and (b) recovering the synthesis gas having reduced amounts of zinc, lead, mercury, and cadmium.

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By converting the volatile metals to their respective sulfides, the metals are converted to a very stable form for handling and disposal. Thus, atmospheric emissions of volatile metals are reduced and disposal is simplified.

Best Mode for Carrying Out the Invention

The particular type of gas stream treated according to the invention is not critical. The gaseous stream is any stream containing zinc, lead, mercury, cadmium, nickel, 5 antimony, or arsenic and which optionally contains other compounds, such as hydrogen cyanide, which react with polysulfides. However, the gaseous stream does not contain compounds which interfere with the reaction between the metals and polysulfide, such as O<sub>2</sub>, found in the gaseous 10 effluent of oxygen-rich coal-fired boilers/furnaces of conventional coal-fired power plants. As used in this specification and appended claims zinc, lead, mercury, cadmium, nickel, antimony, or arsenic means elemental zinc, lead, mercury, cadmium, nickel, antimony, or arsenic or 15 compounds containing these metals. Gaseous streams or effluents particularly suited to the invention include fuel gases produced by gasification procedures. Such gases include fuel or effluent gases derived from the gasification of coal, petroleum, shale, tar sands, etc. Preferably, the 20 stream is a coal or petroleum coke synthesis gas stream.

In such gasification processes, the gaseous effluents are often quenched with water or gaseous liquids. The volatile metals content of the treated gaseous stream will range from trace amounts to about one percent by 25 volume. Preferably, such content is from about 0.05 ppm by weight to about 10 ppm by weight.

The first step, the contacting step, of the process is preferably done on a continuous basis. That is, the metal-containing gas and polysulfide-containing aqueous 30 solution are both continuously supplied to a contacting zone. The polysulfide-containing solution is added by injection into the gaseous stream or by adding it alone or adding it as part of a scrubbing solution or quenching solution. Preferably, it is added to a scrubber unit, such 35 as a packed column scrubber. The packing is any material, such as stainless steel rings, which is wetted by the polysulfide-containing solution. The flow direction of the

two streams in the scrubber unit is preferably counter-current.

The amount of the polysulfide-containing solution added is an effective amount to convert a substantial portion, e.g., at least 20% by weight, of the volatile metals to their respective sulfides. Normally, the polysulfide-containing aqueous solution has at least a stoichiometric amount of polysulfide sulfur with respect to the zinc, lead, mercury, and cadmium. Preferably, up to 5 to 10 times the stoichiometric amount of polysulfide sulfur is present. Elemental sulfur is supplied to the contact zone as needed to maintain this concentration.

Typical concentrations of the polysulfide in the polysulfide-containing solution are from about 5 ppm to 15 about 1,000 ppm. Preferable concentrations are from about 15 ppm to about 50 ppm. Where compounds, other than zinc, lead, mercury, cadmium, nickel, antimony, or arsenic, are present which react with the sulfides, higher concentrations of polysulfide must be used since some sulfides will react 20 with the other compounds.

The contacting occurs at effective conditions for the conversion of the volatile metals to their respective sulfides. Contacting temperature is preferably from ambient temperature to not more than about 200°F. Contacting pressure is from about 1 atmosphere to about 30 atmospheres. The pH of the contacting solution is from about 7 to about 25 9, preferably from about 7.5 to about 9.5. The gas-liquid contacting time is from about 0.1 minute to about 1 minute, preferable from about 0.2 minute to about 0.5 minute. The residence time of the polysulfide-containing solution is from about 30 10 minutes to about 60 minutes or longer. Those skilled in the art are capable of selecting suitable conventional contacting or scrubbing devices to carry out the contacting or scrubbing.

Any water-soluble polysulfide is suitable which does not contribute to the volatile metal concentration or add other environmentally hazardous compounds to the gaseous

stream. Ammonium polysulfide, sodium polysulfide, and mixtures thereof are preferred polysulfides. Where ammonium polysulfide is used and the pH is adjusted by the addition of an alkali such as NaOH, those skilled in the art will recognize that a mixture of polysulfides is also present.

We have now found that the sulfides of the volatile metals, which are largely insoluble in water, will concentrate on the packing material in the packed scrubbing bed. The packing material is then regenerated or disposed of in an environmentally safe manner. The synthesis gas is recovered having reduced amounts of volatile metals including reduced amounts of zinc, lead, mercury, and cadmium.

#### Illustrative Embodiment and Comparative Example

##### A. Illustrative Embodiment

In one coal gasification process, following the process of this invention, a bituminous coal feed, Blacksville #2 coal, was gasified to produce volatile-metal containing synthesis gas in a 250-ton per day entrained flow gasifier. After quenching, cooling, and solids separation, the synthesis gas was passed through a packed column scrubbing unit containing stainless steel packing rings having a 2-inch diameter. An aqueous solution containing 100 ppm sodium polysulfide was fed to the scrubber in countercurrent flow. The flow rate of synthesis gas was 65,000 lbs/hr. The polysulfide solution was recirculated at a flow rate of 140,000 lbs/hr. The liquid to gas flow rate was 2.1:1. The gas-liquid contact time was 0.1 minute. The residence time of the polysulfide solution was 60 minutes. The temperature of the contacting zone was 200°F. The pressure was 280 psig. The pH was 8.5.

##### B. Comparative Example

In a different coal gasifier unit a comparative example was run which did not utilize the polysulfide scrubbing in the process of this invention. The process otherwise operated the same and under the same conditions and with the same feed as the illustrative embodiment above

except for the following differences. A 50-ton per day entrained flow gasifier was used. The flow rate of synthesis gas was 13,000 lbs/hr. Water, without any polysulfide, was recirculated in the scrubber at a flow rate of 28,000 lbs/hr. The pH was 7.2.

In the Table below the concentration of volatile metals is given with and without scrubbing.

REMOVAL OF VOLATILE METALS FROM SYNTHESIS GAS STREAM			
	Type of Volatile Metal	Conc. Without (ppmw)	Conc. With (ppmw)
10	Zinc	1	0.013
	Lead	0.7	0.048
	Mercury	0.14	<0.007
	Cadmium	0.016	<0.003
	Nickel	0.062	<0.003
	Antimony	0.032	<0.003
	Arsenic	0.121	0.007

As shown by the Table, the polysulfide solution effectively reduces the amount of volatile metals in the synthesis gas stream.

CLAIMS

What is claimed is:

1. A process for removing volatile metals from a synthesis gas stream comprising:
  - (a) contacting in a contacting zone a synthesis gas stream containing zinc, lead, mercury, and cadmium with a polysulfide-containing aqueous solution under conditions to convert said zinc, lead, mercury, and cadmium to their respective metal sulfides; and
  - (b) recovering said synthesis gas having reduced amounts of zinc, lead, mercury, and cadmium.
2. The process according to claim 1 wherein said synthesis gas comprises a stream derived from the gasification of petroleum coke.
3. The process according to claim 1 wherein said synthesis gas comprises a stream derived from the gasification of coal.
4. The process according to claim 3 wherein said synthesis gas stream further comprises nickel and said contacting further produces nickel sulfide.
5. The process according to claim 3 wherein said synthesis gas stream further comprises antimony and said contacting further produces antimony sulfide.
6. The process according to claim 3 wherein said synthesis gas stream further comprises arsenic and said contacting further produces arsenic sulfide.
7. The process according to claim 1 wherein the amount of polysulfide-containing solution supplied in step (a) contains at least a stoichiometric amount of polysulfide sulfur with respect to said zinc, lead, mercury, and cadmium.
8. The process according to claim 7 wherein said polysulfide is ammonium polysulfide or sodium polysulfide.
9. The process according to claim 1 wherein said polysulfide-containing solution comprises from about 50 ppm to about 10,000 ppm polysulfide.

10. The process according to claim 9 wherein said polysulfide-containing solution comprises from about 150 ppm to about 500 ppm polysulfide.

11. The process according to claim 9 wherein said contacting is at a temperature of from about ambient to not more than about 200°F.

12. The process according to claim 11 wherein said contacting is at a pressure of from about 1 atmosphere to about 30 atmospheres.

13. The process according to claim 2 wherein said contacting is at a pH of from about 7 to about 9.

14. The process according to claim 13 wherein said contacting is at a pH of from about 7.5 to about 8.5.

15. The process according to claim 2 wherein a portion of said zinc, lead, mercury, and cadmium is in the elemental form as gaseous species or fine particulates.

16. A process for removing volatile metals from a synthesis gas stream comprising:

- (a) contacting in a contacting zone a synthesis gas stream containing zinc, lead, mercury, and cadmium with a polysulfide-containing aqueous solution, containing from about 150 ppm to about 500 ppm polysulfide, under conditions to convert said zinc, lead, mercury, and cadmium, wherein said contacting is at a pH of from about 7.5 to about 8.5, at a temperature of from about ambient to not more than about 200°F, and at a pressure from about 1 atmosphere to about 30 atmospheres;
- (b) thereby producing the respective metal sulfides of said zinc, lead, mercury, and cadmium; and
- (c) recovering said synthesis gas having reduced amounts of zinc, lead, mercury, and cadmium.

## INTERNATIONAL SEARCH REPORT

Int'l. Application No

PCT/US 94/03775

A. CLASSIFICATION OF SUBJECT MATTER  
 IPC 5 B01D53/34 B01D53/14 C10K1/10

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
 IPC 5 B01D C10K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US,A,5 034 203 (MOBIL OIL CORP.) 23 July 1991 see the whole document	1,7-16
Y	---	2-4
P,X	DATABASE WPI Section Ch, Week 9418, Derwent Publications Ltd., London, GB; Class A41, AN 94-147100 & JP,A,6 091 129 (JGC CORP) 5 April 1994 see abstract	1,7,8
Y	FR,A,2 380 339 (METALLGESELLSCHAFT AG) 8 September 1978 see page 1, line 1 - line 11 see page 3, line 25 - page 5, line 14; claims 1-3	2-4
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	-/-	

 Further documents are listed in the continuation of box C. Patent family members are listed in annex.

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Date of the actual completion of the international search  22 July 1994	Date of mailing of the international search report  01.08.94
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE,A,41 23 907 (GEA WIEGAND GMBH) 21 January 1993 see the whole document ---	1,7,8, 15,16
A	US,A,4 671 803 (TEXACO DEVELOPMENT CORP.) 9 June 1987 see the whole document ---	1-3,5,6, 11,12,16
A	US,A,4 505 881 (SHELL OIL CO.) 19 March 1985 see the whole document ---	1-3,7,8, 11-14,16
A	US,A,4 748 141 (SHELL OIL CO.) 31 May 1988 see the whole document -----	1-3,16

**INTERNATIONAL SEARCH REPORT**  
Information on patent family members

International Application No  
**PCT/US 94/03775**

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